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Mössbauer Study of Tin(II) Chloride Hydroxide and Tin(II) Hydroxide Oxide

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The precipitates obtained by addition of a solution of $NaHCO_3$ to a solution of $SnCl_2$ at various pH were studied by thermal analysis, Mössbauer spectroscopy, and X-ray powder diffraction. The formula of the tin(II) chloride hydroxide precipitate obtained in the range of pH 1.9—2.5 was determined as $2SnO \cdot SnCl_2 \cdot H_2O$, or $Sn_3O(OH)_2Cl_2$, and the formula of the hydroxide oxide obtained in the range of pH 7.0—7.7 was $3SnO \cdot 2H_2O$, or $Sn_3(OH)_4O$. In the intermediate pH range, the chloride ions were gradually replaced by hydroxide ions. The dehydration of hydroxide oxide to produce SnO occurred in two stages and the disproportionation reaction of SnO to SnO_2 and β-tin proceeded *via* Sn_2O_3.

When a solution of an alkali is added to a solution of a tin(II) compound, in the absence of a strong-donor anion, the precipitate is a basic chloride salt at first, but further addition of hydroxide ion results in the gradual replacement of the anion by hydroxide and finally, the precipitate turns into a hydroxide oxide. These tin(II) chloride hydroxide and hydroxide oxide have been studied by many workers and various formulas have been reported.[1-4] Among others, Donaldson *et al.* have reported that the only one preparable as a clearly defined crystalline phase of tin(II) chloride hydroxide from aqueous solution is $Sn_4(OH)_6Cl_2$[2] and that the most probable composition of the tin(II) hydroxide oxide is $5SnO \cdot H_2O$, or $Sn_5O_3(OH)_4$.[3] Howie and Moser obtained single crystals of tin(II) hydroxide oxide, they were able to establish the crystal structure by X-ray diffraction and determined the formula to be $3SnO \cdot H_2O$.[4] Furthermore, Honnick and Zuckerman synthesized tin(II) hydroxide, $Sn(OH)_2$, by an anhydrous, organometallic method.[5]

In this study, the precipitates obtained on addition of a solution of $NaHCO_3$ to a solution of $SnCl_2$ as a function of pH were examined by thermal analysis, X-ray powder diffraction, and Mössbauer spectroscopy. The thermal behavior of the tin(II) chloride hydroxide and hydroxide oxide was also examined by quenching, X-ray powder diffraction, and Mössbauer spectroscopy.

Experimental

Preparation of Tin(II) Chloride Hydroxide and Tin(II) Hydroxide Oxide. Tin(II) chloride dihydrate (2.5 g) was dissolved in 8 mol dm^{-3}-HCl (3 ml). The saturated aqueous solution of $NaHCO_3$ was added to the solution under an atmosphere of nitrogen until the pH of the solution reached the predesignated value, while the solution was stirred by means of ultrasonic waves. The white precipitates filtered off were washed throughly with de-airated water, ethanol, and diethyl ether successively under nitrogen and dried for 2 d in vacuum over potassium hydroxide pellets.

Thermal Decomposition Products of Tin(II) Chloride Hydroxide and Tin(II) Hydroxide Oxide. The samples of the thermal decomposition products for the study of the thermal behavior of the tin(II) chloride hydroxide and hydroxide oxide were prepared by heating the material in a furnace with a nitrogen gas flow up to a temperature where the reaction occurred in the DTA curve and then rapidly cooled to room temperature.

Measurements. TG and DTA heating-curves were recorded simultaneously using a Sinku-riko TGD-5000 RH instrument by heating the sample at a rate of 10 °C min^{-1} in flowing nitrogen gas. About a 10-mg sample was placed in a cell and α-alumina was used as the reference material. The Mössbauer spectra were measured using a constant acceleration type spectrometer and the accuracy was within 0.05 mm s^{-1}. The γ-ray source of calcium stannate was used at room temperature and the sample was cooled to 93 K in a liquid nitrogen cryostat. The velocity scale was calibrated against the spectra of $BaSnO_3$ and β-Sn at room temperature. All isomer shifts are reported relative to $BaSnO_3$. Mössbauer parameters were deduced from Lorentzian curves computer-fitted to the spectra by the least squares method.

Results and Discussion

TG-DTA curves of the precipitate obtained at pH 2.4 are shown in Fig. 1. The weight loss occurs in two stages; the first stage at about 170 °C is dehydration and the second stage over the range 350—550 °C is volatilization of $SnCl_2$. The TG-DTA curves of the precipitates obtained at pH 7.2 and 7.5 are shown in Figs. 2 and 3, respectively. In these cases, the dehydration occurs in two stages. It is to be noted that if the precipitates were obtained with stirring other than

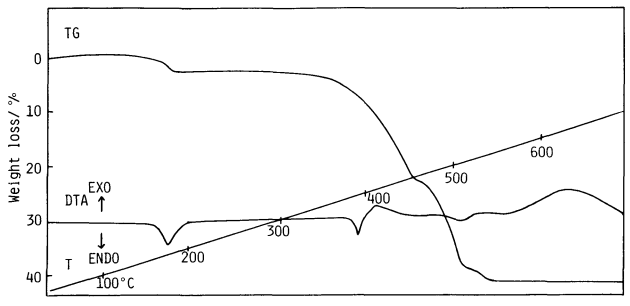

Fig. 1. The TG-DTA curves of tin(II) chloride hydroxide precipitated at pH 2.4.

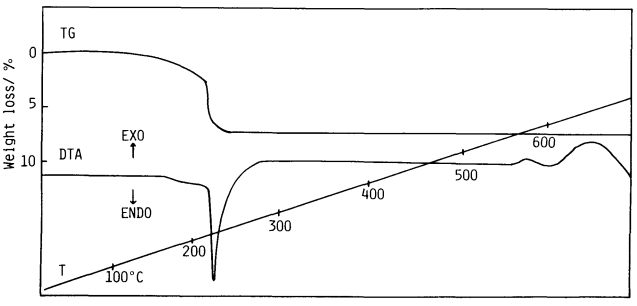

Fig. 2. The TG-DTA curves of tin(II) hydroxide oxide precipitated at pH 7.2.

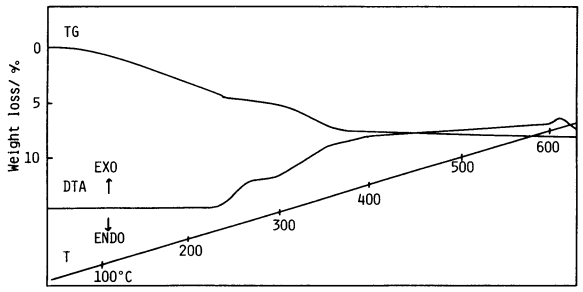

Fig. 3. The TG-DTA curves of tin(II) hydroxide oxide precipitated at pH 7.5.

Table 1. Thermal analysis data and Mössbauer parameters of the precipitates with pH

pH	Thermal analysis (wt%)			Mössbauer parameters	
	H_2O	$SnCl_2$	SnO	δ/mm s^{-1}	Δ/mm s^{-1}
1.90	4.2	39.0	56.8	3.33	1.91
2.05	4.0	39.0	57.0	3.30	1.92
2.10	4.0	37.0	59.0	3.30	1.93
2.40	4.0	39.2	56.8	3.35	1.85
2.50	4.0	32.0	64.0	3.31	1.91
2.55	6.4	12.5	81.8	2.99	2.19
2.60	7.2	20.0	72.8	3.12	2.10
2.70	8.5	17.5	74.0	3.01	2.17
2.80	5.0	12.5	82.5	2.99	2.18
3.10	4.7	13.5	81.8	2.93	2.21
3.80	5.5	10.0	84.5	2.98	2.19
4.90	5.0	4.2	90.8	2.90	2.25
5.80	5.5	2.5	93.0	2.88	2.17
6.30	6.0	0.5	94.0	2.93	2.25
6.70	7.2	0.5	92.7	2.92	2.30
6.80	7.2	0.5	92.7	2.93	2.28
6.90	8.0	0.2	91.8	2.93	2.29
7.00	7.7	0.3	92.0	2.92	2.31
7.20	8.0	0.0	92.0	2.91	2.28
7.40	8.0	0.0	92.0	2.90	2.32
7.50	7.8	0.0	92.2	2.88	2.32
7.70	7.8	0.0	92.2	2.93	2.28

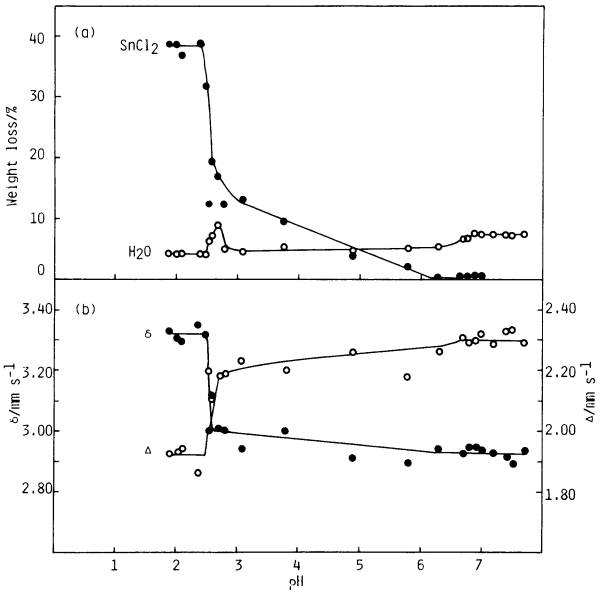

Fig. 4. The plots of the analytical data (a) and Mössbauer parameters (b) against pH.

by means of ultrasonic waves, the reliable weight loss curves could not be recorded. The analytical data, including the residual SnO from the TG curves over the pH range 1.90—7.70, are listed in Table 1, along with the Mössbauer parameters. The variations of the values against pH are schematically shown in Fig. 4.

From the analytical data in Table 1, the precipitates obtained over the pH range 1.90—2.50 are tin(II) chloride hydroxide, the formula of which is $2SnO \cdot SnCl_2 \cdot H_2O$, or $Sn_3O(OH)_2Cl_2$. The formula of the tin(II) hydroxide oxide precipitates obtained over the pH range 7.20—7.70 is $3SnO \cdot 2H_2O$, or $Sn_3(OH)_4O$. In disagreement with these formulas, Donaldson *et al.* have previously reported the formula $3SnO \cdot SnCl_2 \cdot H_2O$, or $Sn_4(OH)_6Cl_2$, for the crystalline basic chloride which was obtained by addition of ammonia solution to the solution of tin(II) chloride over the pH range1.14—4.5.[2] They have also reported the formula $5SnO \cdot 2H_2O$, or $Sn_5O_3(OH)_4$, for the tin(II) hydroxide oxide which was prepared by addition of an oxygen free solution of alkali or alkali carbonate to oxygen free solutions of tin(II) sulfate, under nitrogen, until the pH of the solution was between 10 and 12.[3] Accordingly, the Mössbauer parameters in Table 1 and the X-ray diffraction diagrams shown in Figs. 6(a), 8(a), and 10(a) are not in agreement with the data of Donaldson *et al.*[2,3,6] Another formula $3SnO \cdot H_2O$ has been reported by Howie and Moser for the single crystals of hydroxide oxide obtained from stannous perchlorate solution by prolonged passage of oxygen-free nitrogen containing a very low concentration of ammonia.[4]

Tin(II) ions complex with Cl^- in solution containing hydrochloric acid; Haight *et al.* reported the relative population of various $SnCl_n^{2-n}$ complexes at ion strength 4.0 and varying chloride ion concentration.[7] On the other hand, bivalent tin ion can hydrolyze water and Tobias found that the main product of hydrolysis is the cyclic polynuclear ion $Sn_3(OH)_4^{2+}$.[8] By neutralizing the solution of $SnCl_2$ in hydrochloric acid with $NaHCO_3$, tin(II) ions complexed with Cl^- hydrolyze water and culminate in the precipitation of the tin(II) chloride hydroxide at pH 1.9—2.5. With increasing OH^- concentration, the chloride ions are replaced by hydroxide ions, the fraction of the $Sn_3(OH)_4^{2+}$ ions increase, and finally, the single phase of $Sn_3(OH)_4O$ precipitates in the pH range above 7.0 according to the reaction:

$$Sn_3(OH)_4^{2+} + 2(OH)^- \rightarrow Sn_3(OH)_4O + H_2O.$$

The Mössbauer parameters, both the isomer shift and quadrupole splitting, of the precipitates obtained over the pH range 2.55—4.90 changed with pH from the values of the chloride hydroxide to the hydroxide oxide. Accordingly the materials are not a mixture of the chloride hydroxide and hydroxide oxide. The Cl^- ligands of Sn^{II} are gradually replaced by OH^- as the pH rises. The X-ray diagrams of those materials gave weak patterns similar to those of $Sn_3(OH)_4O$.

The Mössbauer spectra and X-ray powder diagrams of tin(II) chloride hydroxide obtained at pH 2.4 and the thermal decomposition products obtained by heating to higher temperatures are shown in Figs.5 and 6, respectively. The Mössbauer parameters deduced from the spectra and existing phases are shown in Table 2.

The dehydrated product heated up to 200 °C changes to contain two species of Sn^{II}, which are equivalent in the initial compound. The product with smaller isomer shift is coordinated with more oxygen ligands; the other product with larger shift is coordinated with more chlorine ligands. The endothermic peak at 390 °C in the DTA curve in Fig. 1 is a melting reaction because the samples heated up to 370 and 420 °C gave similar Mössbauer parameters and X-ray diagrams, as is shown

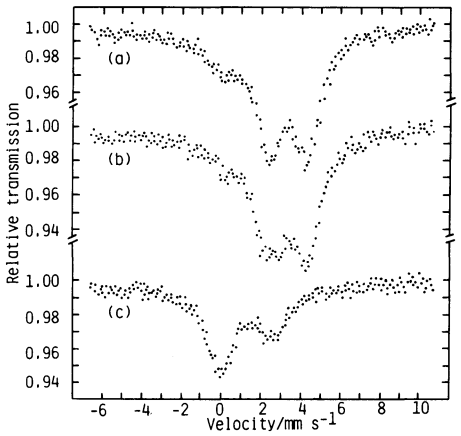

Fig. 5. Mössbauer spectra of tin(II) chloride hydroxide precipitated at pH 2.4 (a), and the thermal decomposition products by heating up to, (b) 200 °C; (c) 700 °C.

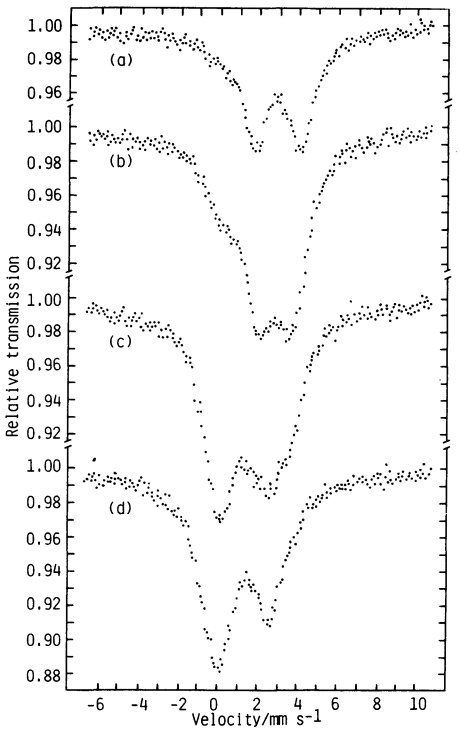

Fig. 7. Mössbauer spectra of tin(II) hydroxide oxide precipitated at pH 7.2 (a), and the thermal decomposition products by heating up to, (b) 260 °C; (c) 600 °C; (d) 700 °C.

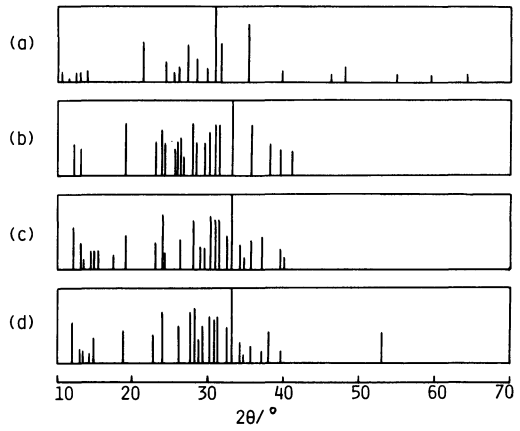

Fig. 6. X-Ray powder diagrams of tin(II) chloride hydroxide precipitated at pH 2.4 (a), and the thermal decomposition products by heating up to, (b) 200 °C; (c) 370 °C; (d) 420 °C.

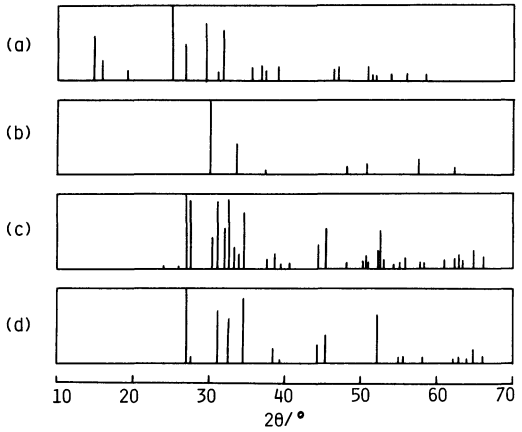

Fig. 8. X-Ray powder diagrams of tin(II) hydroxide oxide precipitated at pH 7.2 (a), and the thermal decomposition products by heating up to, (b) 260 °C; (c) 600 °C; (d) 700 °C.

Table 2. Mössbauer parameters of tin(II) chloride hydroxide precipitated at pH 2.4 and the thermal decomposition products by heating up to 200, 370, 420, and 700 °C

Temp	Sn^{II}		Sn^{IV}	Sn^{0}	Existing phase
°C	δ/mm s^{-1}	Δ/mm s^{-1}	δ/mm s^{-1}	δ/mm s^{-1}	
20	3.35	1.85			$Sn_3O(OH)_2Cl_2$
200	3.39	2.39			$Sn_3O_2Cl_2$
	3.52	1.21			
370	3.09	2.16			$Sn_3O_2Cl_2$
	3.61	1.71			
420	3.12	2.05			$Sn_3O_2Cl_2$
	3.73	1.59			
700			0.00	2.54	SnO_2, β-Sn

in Table 2 and Fig. 6, respectively. The final decomposition product heated to 700 °C is a mixture of tin(IV) oxide and β-tin as a consequence of the disproportionation reaction of SnO, which was observed in the DTA curve as the broad peak at about 600 °C.

The Mössbauer spectra and X-ray powder diagrams of tin(II) hydroxide oxide obtained at pH 7.2 and the thermal decomposition products obtained by heating to 260, 600, and 700 °C are shown in Figs. 7 and 8, respectively. The Mössbauer parameters and existing phases are shown in Table 3. The dehydration product heated to 260 °C was SnO, the product heated to 600 °C was a mixture of Sn_2O_3 and β-tin, and the final product obtained by heated to 700 °C is a mixture of SnO_2 and β-tin. Thus, in this hydroxide oxide, the disproportionation of SnO to SnO_2 and β-Sn occurs in two stages *via* Sn_2O_3 and the stages of the thermal decomposition are confirmed as :

$$2Sn_3(OH)_4O \rightarrow 6SnO \rightarrow 2Sn_2O_3 + 2\beta\text{-}Sn \rightarrow 3SnO_2 + 3\beta\text{-}Sn$$

The Mössbauer parameters and X-ray diagrams of tin(II) hydroxide oxide obtained at pH 7.5 and the thermal decomposition products by heating to 250, 420, 620, and 640 °C are shown in Figs. 9 and 10, respectively. The Mössbauer parameters and the existing phases are shown in Table 4. In the Mössbauer spectrum of Fig. 9(a), the area ratio of the tin(IV) impurity to the total was 20%. This suggests that if the

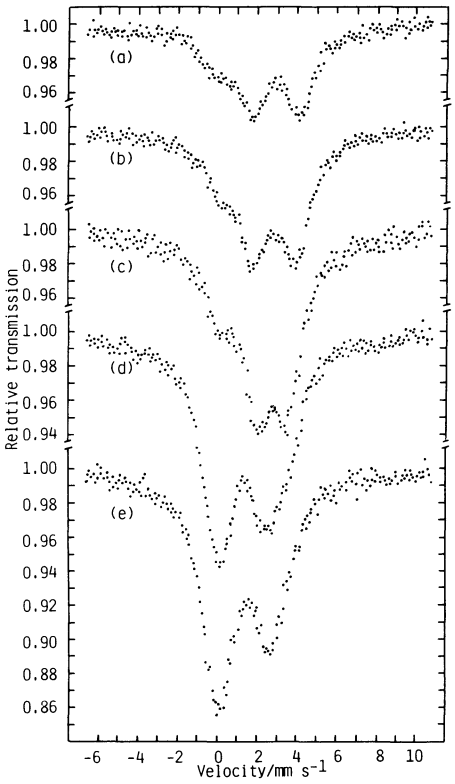

Fig. 9. Mössbauer spectra of tin(II) hydroxide oxide precipitated at pH 7.5 (a), and the thermal decomposition products by heating up to, (b) 250 °C; (c) 420 °C; (d) 620 °C; (e) 640 °C.

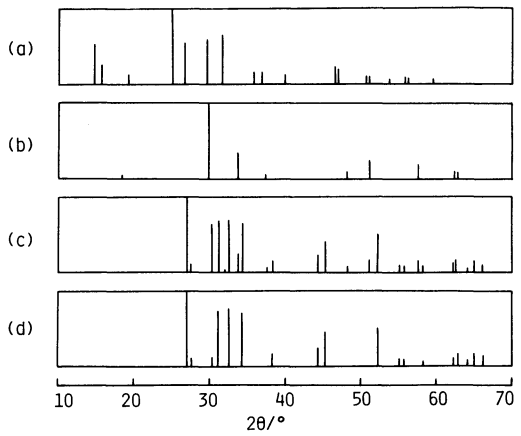

Fig. 10. X-Ray powder diagrams of tin(II) hydroxide oxide precipitated at pH 7.5 (a), and the thermal decomposition products by heating up to, (b) 370 °C; (c) 620 °C; (d) 640 °C.

Table 3. Mössbauer parameters of tin(II) hydroxide oxide precipitated at pH 7.2 and the thermal decomposition products by heating up to 260, 600, and 700 °C

Temp	Sn^{II}		Sn^{IV}	Sn^0	Existing phase
°C	δ/mm s^{-1}	Δ/mm s^{-1}	δ/mm s^{-1}	δ/mm s^{-1}	
20	2.91	2.28			$Sn_3(OH)_4O$
260	2.76	1.62			blue-black SnO
600	2.54	1.94	0.00	2.50	Sn_2O_3, β-Sn
700			0.02	2.66	SnO_2, β-Sn

Table 4. Mössbauer parameters of tin(II) hydroxide oxide precipitated at pH 7.5 and the thermal decomposition products by heating up to 250, 420, 620, and 640 °C

Temp	Sn^{II}		Sn^{IV}	Sn^0	Existing phase
°C	δ/mm s^{-1}	Δ/mm s^{-1}	δ/mm s^{-1}	δ/mm s^{-1}	
20	2.88	2.32			$Sn_3(OH)_4O$
250	2.83	2.06			amorphous
420	2.76	1.50			blue-black SnO
620	2.83	1.64	0.04	2.70	blue-black SnO, SnO_2, β-Sn
640			0.01	2.67	SnO_2, β-Sn

pH rises above 7.0, the oxidation of tin(II) to tin(IV) proceeds with the increase of pH and the stannic tin is involved in the lattice of hydroxide oxide. The product heated to 250 °C, in which the first stage dehydration occurred, gave an amorphous X-ray diagram. This orange amorphous material was stable under an atmosphere of air for two weeks or more in diagreement with the previous report of Donaldson *et al.*[3] The second stage of the dehydration proceeds slowly over the temperature range 250—380 °C. The disproportionation reaction of SnO, which was observed as two peaks in the DTA curve of the hydroxide oxide obtained at pH 7.2, collapsed into a small single peak and the residual SnO was still observed in the Mössbauer spectrum of the sample heated to 620 °C. The final product was a mixture of SnO_2 and β-Sn and the intermediate Sn_2O_3 was not detected. These differences in the thermal behavior of the tin(II) hydroxide oxide can be ascribed to the change of tin(IV) content with pH.

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